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Immobilized Ionic Liquids as High-Selectivity/ High-Temperature/High-Stability Gas Chromatography Stationary Phases

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Abstract
Ionic liquids (ILs) are a class of nonmolecular solvents in which the cation/anion combination can be easily tuned to provide desired chemical and physical properties. When used as stationary phases in gas–liquid chromatography, ionic liquids exhibit dual nature retention selectivity. That is, they are able to separate polar molecules such as a polar stationary phase and nonpolar molecules such as a nonpolar stationary phase. However, issues such as optimization of the wetting ability of the ionic liquid on fused-silica capillaries, the maximum operating temperatures of the stationary phases, and nonuniform film thickness on the wall of the capillary at high temperatures have limited their use in gas chromatography. As described in this paper, these limitations are overcome by cross-linking a new class of ionic liquid monomers by free radical reactions to provide a more durable and robust stationary phase. By lightly cross-linking the ionic liquid stationary phase using a small amount of free radical initiator, high-efficiency capillary columns were produced that are able to endure high temperatures with little column bleed. Two types of cross-linked IL stationary phases are developed. A partially cross-linked stationary phase allows for high-efficiency separations up to temperatures of ~280 °C. However, by creating a more highly cross-linked stationary phase of geminal dicationic ILs, exclusively, an increase in efficiency is observed at high temperatures allowing for its use over 350 °C. In addition, through the use of solvation thermodynamics and interaction parameters, it was shown that the cross-linking/immobilization of the ionic liquid does not affect the selectivity of the stationary phase thereby preserving its dual nature retention behavior.

Keywords
Crosslinking, Gas chromatography, Optimization, separation, silica, solvents, thickness measurement, liquid monomers, nonmolecular solvents, nonpolar molecules, solvation thermodynamics, ionization of liquids

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Immobilized Ionic Liquids as High-Selectivity/ High-Temperature/High-Stability Gas Chromatography Stationary Phases

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Ionic liquids (ILs) are a class of nonmolecular solvents in which the cation/anion combination can be easily tuned to provide desired chemical and physical properties. When used as stationary phases in gas−liquid chromatography, ionic liquids exhibit dual nature retention selectivity. That is, they are able to separate polar molecules such as a polar stationary phase and nonpolar molecules such as a nonpolar stationary phase. However, issues such as optimization of the wetting ability of the ionic liquid on fused-silica capillaries, the maximum operating temperatures of the stationary phases, and nonuniform film thickness on the wall of the capillary at high temperatures have limited their use in gas chromatography. As described in this paper, these limitations are overcome by cross-linking a new class of ionic liquid monomers by free radical reactions to provide a more durable and robust stationary phase. By lightly cross-linking the ionic liquid stationary phase using a small amount of free radical initiator, high-efficiency capillary columns were produced that are able to endure high temperatures with little column bleed. Two types of cross-linked IL stationary phases are developed. A partially cross-linked stationary phase allows for high-efficiency separations up to temperatures of ~280 °C. However, by creating a more highly cross-linked stationary phase of geminal dicationic ILs, exclusively, an increase in efficiency is observed at high temperatures allowing for its use over 350 °C. In addition, through the use of solvation thermodynamics and interaction parameters, it was shown that the cross-linking/immobilization of the ionic liquid does not affect the selectivity of the stationary phase thereby preserving its dual nature retention behavior.

Room-temperature ionic liquids (RTILs), formerly known as molten salts, are a class of nonmolecular ionic solvents with low melting points. Most common RTILs are composed of unsymmetrically substituted nitrogen-containing cations (e.g., imidazole, pyrrolidine, and pyridine) with inorganic anions (e.g., Cl^-, PF_6^-, and BF_4^-). Ambient-temperature ionic liquids based on the 1-alkyl-3-methylimidazolium cation were first reported by Wilkes et. al. in 1982.[1] In the last 5−10 years, ionic liquids with widely varying cations and anions have been synthesized to provide specific physical and chemical characteristics for a variety of applications. With these so-called "designer solvents", the physical properties and solvation interactions of the ionic liquid can be "tuned" by controlling the nature and functionality of the cation or anion. This ability has tremendous advantages, especially when using ionic liquids as solvent systems in organic synthesis[2−10] and in analytical chemistry.[11−18]

Others have stated that ionic liquids possess low to negligible vapor pressures when used as solvents in organic chemistry.[2,5,10] Therefore, there has been interest in using ILs as stationary phases in gas−liquid chromatography.[19−27] Although RTILs are said to possess high volatilization temperatures, it is commonly observed that this is controlled by the cation and anion

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combination.[25,28−29] For example, when 1-butyl-3-methylimidazolium chloride (BMIM-Cl) was coated on a capillary column, its maximum operating temperature was ~165 °C. Beyond this temperature, this RTIL begins to volatilize, decompose, or both, resulting in increasing column bleed.[25] We have recently described a new class of ionic liquids, termed "high-stability ionic liquids", that employ bulky cations and triflate anions that can be used successfully to provide high-efficiency separations at temperatures up to 260 °C.[25] These stationary phases were shown to efficiently separate a wide variety of analyte mixtures including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and chlorinated pesticides.[25] A new class of chiral stationary phases based on chiral ionic liquids also was introduced recently.[26] The *N*,*N*-dimethylephedrinium-based ionic liquids exhibited enantioselective retention for four different classes of chiral analytes: (1) chiral alcohols (including diols), (2) chiral sulfoxides, (3) some chiral epoxides, and (4) acetylated amines.

Many of the early discovered liquid organic salts such as ethylammonium nitrate and ethylpyridinium bromide suffered from low liquid ranges and produced poor chromatographic efficiencies.[19,20] Imidazolium-based RTILs were used as stationary phases and the retention behavior of various molecules were examined on the 1-butyl-3- methylimidazolium hexafluorophosphate (BMIM-PF_6) and BMIM-Cl RTILs.[21] It was at this time that the "dual nature" behavior of RTIL-based stationary phases was described in detail. That is, the stationary phase separates polar molecules as if it was a polar stationary phase and separates nonpolar molecules like a nonpolar stationary phase.

With the advances in producing chiral and achiral ionic liquid-based stationary phases, there remain several issues that have precluded them from being introduced as robust, widely applicable GC columns. Optimizing the wetting ability of ionic liquids on fused-silica capillary walls to produce high-efficiency separations comparable to the best commercially available phases has been problematic. In addition, increasing the maximum operating temperature of these stationary phases to allow for high-temperature separations also is of intense interest. Recently, we developed a series of ultrahigh-stability geminal dicationic liquids.[30] Some of these were shown to be completely stable and nonvolatile liquids over the temperature range of −5 to >400 °C.[30]

One characteristic of most ILs is that their viscosity decreases sharply with increasing temperature. Consequently, at high temperatures, previously uniform IL-coated capillaries can experience film disruption (due to flow, etc.) When a uniformly coated GC capillary slowly changes to a nonuniformly coated entity, the analyte retention times and efficiency tend to decrease. Thus, while the thermal stability of the newest geminal dicationic ILs was exceptional, the integrity of their thin films on capillary walls was not.

To overcome these limitations, this paper describes the immobilization of special synthesized ionic liquid monomers to provide a more durable and robust stationary phase. By lightly cross-linking the ionic liquid stationary phase using a small percentage of free radical initiator, high-efficiency capillary columns were produced that are able to endure high temperatures with little column bleed. It was found that low to moderate temperature separations (30−280 °C) can be carried out with high selectivity and efficiency using special partially cross-linked ionic liquid stationary-phase mixtures. These stationary phases retain their "gelatinous", "semiliquid", amorphous state. For separations conducted at higher temperatures (300−400 °C), more highly cross-linked stationary phases are well-suited to provide high selectivity and efficient separations with low column bleed. The effect of different functionalized RTIL mixtures and initiator concentrations is studied for these two types of stationary phases. The accomplished goal is to maximize their separation efficiency, thermal stability, and column lifetime, without sacrificing the unique selectivity of the RTIL stationary phase.

EXPERIMENTAL SECTION

Materials. 1-Vinylimidazole, 1-bromohexane, 1-bromononane, 1-bromododecane, 1,9-dibromononane, 1,12-dibromododecane, 1-bromo-6-chlorohexane, 1- methylimidazole, *N*-lithiotrifluoromethanesulfonimide, 2,2′-azobisisobutyronitrile (AIBN), dichloromethane, ethyl acetate, and all test solutes were purchased from Aldrich (Milwaukee, WI). Untreated fused-silica capillary tubing (0.25-mm inner diameter), fatty acid methyl ester (FAME), and PAH kits were purchased from Supelco (Bellafonte, PA). Analytical standards of chlorinated pesticides were purchased from Poly-Science Corp. (Niles, IL).

Methods. Structures and physicochemical properties of the monocation monomers and the dication cross-linkers used in this study are shown in Table 1. Monomers **1**, **2**, and **3** were synthesized by reacting 1 molar equiv of 1-vinylimidazole with a slight molar excess of 1-bromohexane, 1-bromononane, and 1-bromododecane, respectively. These reactions were performed at room temperature in round-bottom flasks lined with aluminum foil to prevent thermal/photoinduced polymerization. Care must be taken when synthesizing and purifying these compounds to minimize excess heat/light during reaction or rotoevaporation to prevent premature free radical reaction/polymerization of the ionic liquid. The resulting bromide salt was evaporated under vacuum to remove the excess 1-bromoalkane. Three 15-mL aliquots of ethyl acetate were used to wash the ionic liquid to remove any other impurities. After evaporating the ethyl acetate under vacuum, the bromide salt was dissolved in water and mixed with 1 molar equiv of *N*-lithiotrifluoromethanesulfonimide, also dissolved in water. After stirring for 12 h, the water was removed and the remaining ionic liquid thoroughly washed with water using three 50-mL aliquots of water. A portion of the third aliquot of water was subjected to the silver nitrate test to ensure the absence of silver bromide precipitate. The monomers were then dried under vacuum and then placed under a P_2O_5 vacuum in the absence of light.

The dication cross-linkers were synthesized using a modified procedure recently reported for a series of geminal dicationic ionic liquids.[30] Compound **4** in Table 1 is a mixture of $C_6(vim)_2^{2+}$ (m/z = 272.1), $C_6vm(im)_2^{2+}$ (m/z = 260.1), and $C_6(mim)_2^{2+}$ (m/z = 248.1) in a 1:2:1 molar mixture, respectively, as indicated in the electrospray mass spectrum in Figure 1. When acquired in positive ion mode, the most dominant ions for these three structurally similar compounds appear to be the +1 ion minus a proton.

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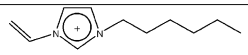
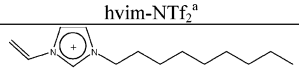
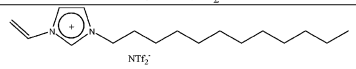
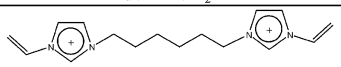
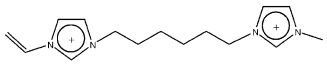
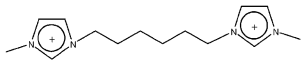
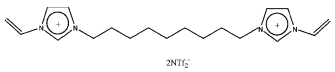
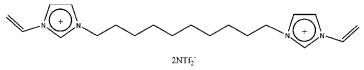
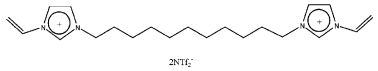
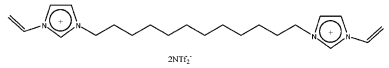
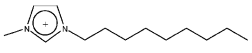
Table 1. Structure and Physicochemical Properties of the Monomers/Cross-linkers Used in This Study

#	Ionic Liquid	Molecular Weight (g/mol)	Density (g/cm^3)	Refractive Index
1	 hvim-NTf_2[a]	459.1	1.36	1.443
2	 nvim-NTf_2[b]	501.2	1.28	1.445
3	 dvim-NTf_2[c]	543.3	1.23	1.448
4	 $C_6(vim)_2$-NTf_2[d]	832.1	1.53	1.449
	 $C_6vm(im)_2$-NTf_2[e]	820.1		
	 $C_6(mim)_2$-NTf_2[f]	808.1		
	$C_6(vim)_2$-NTf_2 : $C_6vm(im)_2$-NTf_2 : $C_6(mim)_2$-NTf_2 1 : 2 : 1			
5	 $C_9(vim)_2$-NTf_2[g]	874.3	1.47	1.457
6	 $C_{10}(vim)_2$-NTf_2[h,*]	888.3	--	--
7	 $C_{11}(vim)_2$-NTf_2[i]	902.3	1.44	1.457
8	 $C_{12}(vim)_2$-NTf_2[j,*]	916.3	1.42	1.458
9	 nmim-NTf_2[k]	489.3	1.30	1.434

[a] 1-Vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl]imidate. [b] 1-Vinyl-3-nonylimidazolium bis[(trifluoromethyl)sulfonyl]imidate. [c] 1-Vinyl-3-dodecylimidazolium bis[(trifluoromethyl)sulfonyl]imidate. [d] 1,6-Di(3-vinylimidazolium)hexane bis[(trifluromethyl)sulfonyl]imidate. [e] 1-(3-Vinylimidazolium)-6-(3′-methylimidazolium)hexane bis[(trifluoromethyl)-sulfonyl]imidate. [f] 1,6-Di(3-methylimidazolium)hexane bis[(trifluoromethyl)sulfonyl]imidate. [g] 1,9-Di(3-vinylimidazolium)nonane bis[(trifluoromethyl)sulfonyl]imidate. [h] 1,10-Di(3-vinylimidazolium)decane bis-[(trifluoromethyl)sulfonyl]imidate. [i] 1,11-Di(3-vinylimidazolium)undecane bis[(trifluoromethyl)sulfonyl]imidate. [j] 1,12-Di(3-vinylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imidate. [k] 1-Nonyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imidate. *Ionic liquids **6** and **8** both exhibit behavior similar to other supercooled ionic liquids. After becoming a supercooled liquid, **8** was observed to have a melting point of 43 °C. However, **6** quickly becomes a solid with a melting point of 61 °C.

Further experiments conducted in our group in which the C-2 proton on the imidazolium ring (see Figure 1 for numbering of ring system) is deuterated indicates that this proton is lost and causes one of the positive charged aromatic rings to neutralize charge and give rise to the +1 ion (data not shown). This mixture was synthesized by reacting 1 molar equiv of 1-bromo-6-chlorohexane with 1 molar equiv of 1-methylimidazole in an ice bath overnight. Subsequently, 1 molar equiv of 1-vinylimidazole was added dropwise over a period of 30 min and the temperature of the mixture increased to 55 °C for 3 h. Three 15-mL aliquots of ethyl acetate were used to extract any excess starting material, and the bromide anion was exchanged for the bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-) anion by reaction of 2 equiv of *N*-lithiotrifluoromethanesulfonimide dissolved in water for every 1 equiv of the cross-linker salt.

In an analogous manner, the remaining cross-linkers **5**, **6**, **7**, and **8** were prepared by reacting 1 molar equiv of the dibromoalkane with 2 molar equiv of 1-vinylimidazole. Compound **9** was prepared by reacting 1 molar equiv of 1-methylimidazole with 1 molar equiv of 1-bromononane at 100 °C for 5 h. Cleanup and metathesis exchange for the NTf_2^- anion was performed as described above for the synthesis of the monomer ionic liquids. ^{1}H NMR spectra (300 Mz recorded in deuterated DMSO) and electrospray mass spectra (positive and negative ion mode) are presented in Supporting Information. Note, these materials are distinctly different from classical polymerized materials such as the commercially available Luviquat copolymers (BASF), which are aqueous solutions of cationic polymers (i.e., polyimidazoles, polyamines, and polyamides) used in a variety of cleansing products and skin care formulations. The polymeric materials discussed in this work are composed solely of cations and anions and exist in a liquid/amorphous state due to the structure/makeup of the cation and anion.[31,32]

Capillaries were coated using the static coating method at 40 °C. Coating solutions of the monomer or cross-linker ionic liquids were prepared at concentrations of 0.20% (w/v) in dichloromethane. Prior to adding the dichloromethane to the monomer or cross-linker mixture, 0.7 mg of AIBN (~3.5 wt %) was added. AIBN is known to undergo decomposition to form cyanoisopropyl radicals, which subsequently produce several products by dimerization, disproportionation reactions, or chain reactions.[33] The thermal decomposition kinetics of AIBN have been well studied using a variety of spectroscopic and polarographic techniques.[34] Van Hook and Tobolsky have proposed a rate expression, based on an Arrhenius plot, for the decomposition of AIBN in solution to be $k_d = 1.58 \times 10^{15} \exp(-30.8 \text{ kcal}/RT)$.[34] For a temperature of 40 °C in which the capillaries are coated with the initiator present in the coating solution, this yields a decomposition rate constant of $\sim 5.07 \times 10^{-7}$ s^{-1}. Due to the fact that this rate constant is so small and that the coating rate is relatively fast, there should be very little polymerization of the monomer/cross-linker mixture during the coating of the capillary.

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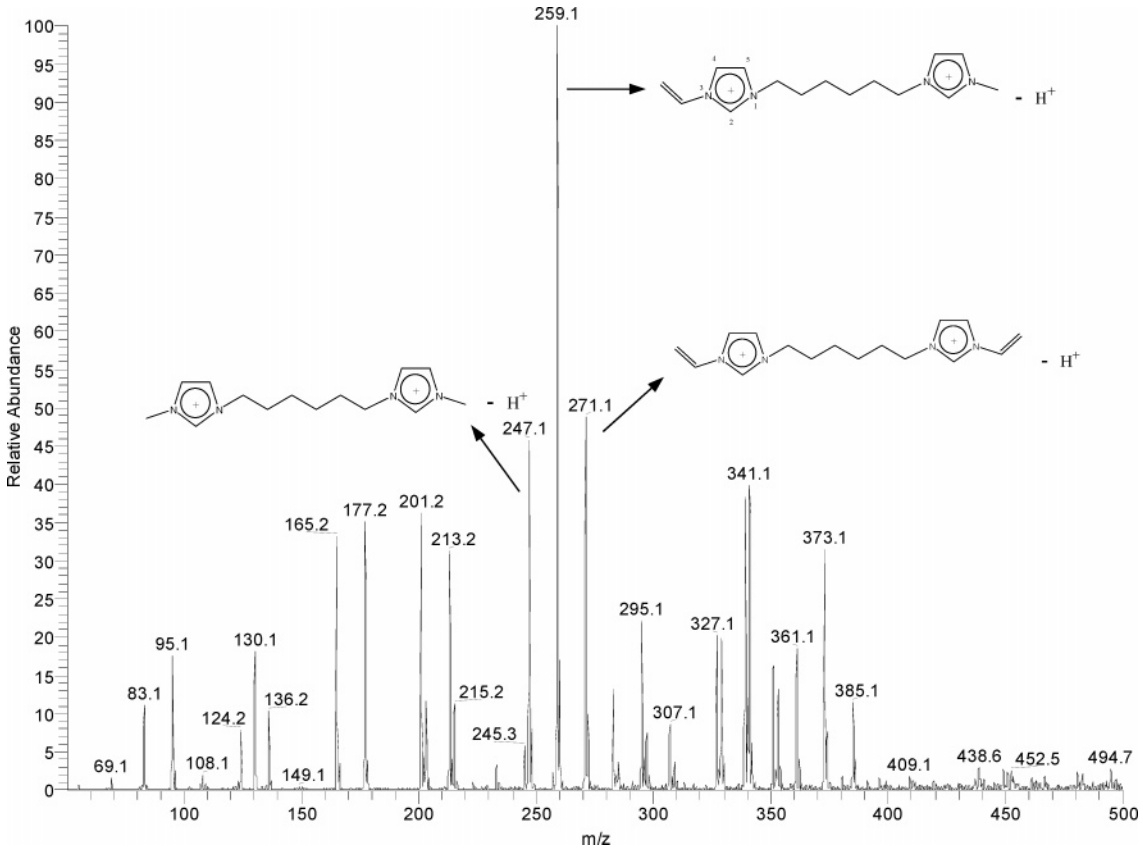

Figure 1. Positive ion electrospray mass spectrum of mixture **4** indicating the relative abundance of the three substituted dications as well as the loss of a proton on the imidazolium ring thereby allowing the formation of the +1 ion.

After coating, the ends of the capillary were flame sealed and the capillary placed in a GC oven and heated from 40 to 80 °C at 1 °C/min. The capillary was then held at 80 °C for 5 h to ensure complete polymerization. Helium carrier gas was then flushed through the capillary at a rate of 1 mL/min and the capillary conditioned from 30 to 120 °C at 3 °C/min and held at 120 °C for 2 h.

Test solutes used to determine interaction parameters and solvation thermodynamics were dissolved in dichloromethane. A Hewlett-Packard model 5890 gas chromatograph and a Hewlett-Packard 6890 series integrator were used for all separations. Split injection and flame ionization detection were utilized with injection and detection temperatures of 250 °C. Helium was used as the carrier gas with a column inlet pressure of 3.1 psi and flow rate of 1.0 mL/min. Methane was used to determine the dead volume of the column. Multiple linear regression analysis and statistical calculations were performed using the program Analyze-it (Microsoft).

Solvation thermodynamics can be determined chromatographically by recognizing that the Gibbs free energy change, $\Delta G°$, of a solute between the mobile phase and the stationary phase can be described by eq 1, where k is the solute retention factor and

$$\Delta G° = -RT \ln(k/\Phi) \qquad (1)$$

Φ is the column phase ratio. The phase ratio, Φ, is defined as the volume of the stationary phase divided by the volume of the mobile phase. A phase ratio of 1.92×10^{-3} based on a 0.12-μm stationary-phase film thickness was calculated for the capillary columns used in this work to determine the solvation thermodynamics. An expression shown in eq 2 can then be derived and illustrates the dependence of enthalpy, $\Delta H°$, and entropy, $\Delta S°$, on the change of the retention factor with temperature:

$$\ln k = -\left(\frac{\Delta H°}{R}\right)\frac{1}{T} + \left[\frac{\Delta S°}{R} + \ln \Phi\right] \qquad (2)$$

A van't Hoff plot of ln k versus $1/T$ allows for the determination of the standard entropy change from the intercept (i.e., $[\Delta S°/R + \ln \Phi]$ term) and the standard enthalpy change from the slope (i.e., $[\Delta H°/R]$ term) thereby describing a solute's transfer from the gas phase to the ionic liquid stationary phase. In this work, the solvation thermodynamics were determined for seven different probe molecules (i.e., fluorophenol, naphthalene, 2-chloroaniline, ethyl phenyl ether, 1-octanol, decane, and nitropropane) on two cross-linked ionic liquid phases and one ionic liquid stationary phase. The aforementioned probe molecules evaluated in this study differ in terms of size and the types of functional groups that they possess. For each probe molecule on each stationary phase, the retention factor was measured three times at each of the six different temperatures to provide an error for each thermodynamic parameter. The probe molecule retention factors were determined at six different temperatures to obtain the highest possible correlation coefficient (>0.989).

Previously we characterized a large number of room-temperature ionic liquids in terms of multiple solvation interactions using

the solvation parameter model, shown in eq 3.[35] This approach utilizes inverse gas−liquid chromatography and allows the use of a large number of probe molecules to deconvolute solute retention interms of the type and magnitude of individual solvation interactions. The solute descriptors (R_2, π_2^H, α_2^H, β_2^H, log L^{16}) from eq 3

$$\log k = c + rR_2 + s\pi_2^{\mathrm{H}} + a\alpha_2^{\mathrm{H}} + b\beta_2^{\mathrm{H}} + l \log L^{16} \quad (3)$$

are obtained from the literature for many probe molecules containing a variety of functional groups.[36] The retention factor is determined chromatographically. The solute descriptors and retention factors are subjected to multiple linear regression analysis to obtain the interaction parameter coefficients (r, s, a, b, l), which ultimately characterize the stationary phase: r is the ability of the RTIL to interact with π and n electrons of the solute, s is a measure of the dipolarity/polarizability of the RTIL, a defines the RTIL hydrogen bond basicity, b is a measure of the hydrogen bond acidity, and l refers to the ability of the RTIL to separate adjacent members of a homologous series.[37]

RESULTS AND DISCUSSION

An optimum, constant stationary phase film thickness must be selected for this study. Too thin of a film gives insufficient wall coverage allowing for interfacial adsorption of analyte molecules whereas too thick a film may result in poor efficiency. Equation 4 can be used to approximate the stationary phase film thickness for gas chromatographic capillaries coated by the static coating method,[38]

$$d_f = d_c c/400 \quad (4)$$

where d_f is the film thickness of the ionic liquid stationary phase in micrometers, d_c is the diameter of the capillary (in micrometers), and c is the percentage by weight concentration of the stationary phase dissolved in an appropriate solvent. Figure 2 shows the effect of 1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl] imidate film thickness on the peak efficiency of naphthalene at 100 °C. As the plot clearly demonstrates, the highest efficiency separations were carried out with a film thickness of ∼0.07 μm (0.10% w/v of ionic liquid in dichloromethane) while the worst efficiency separations were obtained on columns with a film thickness of ∼0.21 μm (0.33% w/v). Given these results, all subsequent capillaries used in this work were coated with a 0.20% (w/v) coating solution yielding a film thickness of ∼0.125 μm.

Optimization of Cross-Linked Stationary-Phase Composition. The goal of this work was to produce partially cross-linked ionic liquid stationary phases that produce high-efficiency separations with low column bleed and with sustained coating integrity at high temperatures. This was accomplished by dissolving various "new unsaturated IL monomers" in dichloromethane with optimized amounts of AIBN initiator, coating them on the inner wall of the capillary, and then carrying out a thermally induced free radical reaction (see Experimental Section). The columns were then evaluated by implementing seven different temperature programs, as shown in Table 2. The temperature programs in this work were chosen in a manner to evaluate the effect of column conditioning temperature on the stationary-phase separation efficiency and thermal stability. To accomplish this, the initial temperature program was started at 30 °C and heated to 120 °C using a 3 °C/min temperature ramp. Subsequent programs started at slightly lower temperatures than the preceding program's high-temperature limit and ended at significantly higher temperatures with hold times between 2 and 5 h. As the temperature programs achieved higher column temperatures (∼360−380 °C), slight column bleed was observed and lower hold times were employed. By using a large number of temperature programs, the temperature range in which the separation efficiency of the immobilized IL begins to decrease drastically was easily identified. After conditioning the column to a certain temperature (see temperature ramps in Table 2), an efficiency test was performed at 100 °C using naphthalene. After the efficiency test was carried out, the next temperature ramp was initiated and followed by the identical test of stationary-phase efficiency at 100 °C.

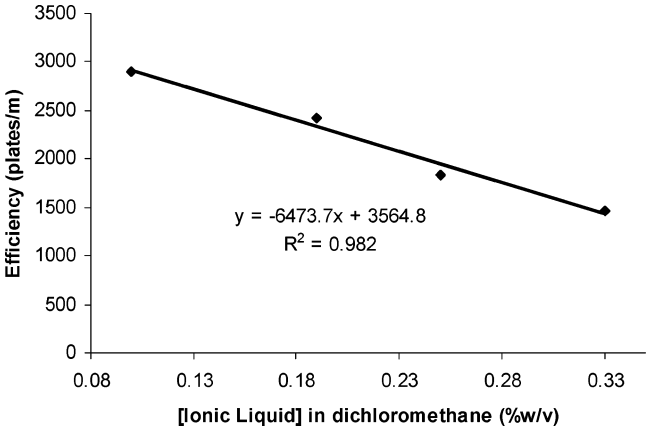

Figure 2. Plot illustrating the effect of 1-vinyl-3-hexylimidazolium bis[(trifluoromethane)sulfonyl]imidate film thickness on the peak efficiency (theoretical plates/meter) of naphthalene at 100 °C. Each column was prepared by subjecting the appropriate concentration of stationary phase to free radical reaction using 3.5 wt % AIBN as described in the Experimental Section.

Using the ionic liquids in Table 1, a variety of free radical cross-linking experiments were carried out in chloroform following the method of Muldoon and Gordon[39] to determine which ratios of monocationic/cross-linker monomers result in copolymers that possess the ideal properties for a GC stationary phase. For example, some copolymers (i.e., formed from monomers **1** and **5**) containing only a few percent by weight cross-linker resemble gumlike polysiloxane phases.[40] However, other highly cross-linked copolymers formed hard plastics and are therefore undesirable for gas−liquid chromatographic separations.[40]

Performance of Monocationic Linear IL Polymers. Monocationic monomer ionic liquids **1**, **2**, and **3** contain the 1-vinylimi-

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(39) Muldoon, M. J.; Gordon, C. M. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3865−3869.
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Table 2. Effect of Monomer Structure and Degree of Cross-Linking on Stationary-Phase Efficiency (Theoretical Plates/Meter) as a Function of Conditioning Temperature

	monocationic linear ionic liquid polymers[a]			partially cross-linked ionic liquid matrix[a]								cross-linked ionic liquid matrix[a]		
	0.20% **1**	0.20% **2**	0.20% **3**	0.20% **4**	0.10% **1** 0.10% **4**	0.15% **1** 0.05% **4**	0.05% **1** 0.15% **4**	0.10% **1** 0.10% **5**	0.10% **2** 0.10% **4**	0.10% **2** 0.10% **5**	0.10% **3** 0.10% **4**	0.20% **5**	0.20% $C_{9-12}(vim)_2$-NTf_2	0.10% **1** 0.10% $C_{9-12}(vim)_2$-NTf_2
30−120 °C 3 °C/min hold 2 h	2813	2429	1860	2926	2916	2714	1768	3660	2938	3566	2957	3206	3189	3155
100−200 °C 3 °C/min hold 5 h	2415	2322	1694	2426	2769	2085	1679	3301	2775	3277	2872	3019	2634	2379
150−250 °C 3 °C/min hold 3 h	2172	2026	1706	1945	2639	2156	1827	2743	2449	3016	2787	2469	1963	1598
200−285 °C 3 °C/min hold 2 h	1778	1677	1100	1710	2180	2047	1623	2088	2302	2536	2361	1554	898	771
200−300 °C 3 °C/min hold 1 h	1542	1432	1090	1517	1835	1626	1226	1419	2058	2024	2157	1334	941	554
200−350 °C 3 °C/min hold 1 h	197	142	120	1365	417	433	719	1119	523	146	340	2101	1891	950
200−380 °C 3 °C/min hold 20 min				193				291				503	269	239

[a] Ionic liquid polymer formed using 3.5% AIBN.

dazolium cation with hexyl, nonyl, and dodecyl alkyl chains, respectively. When polymerized, these ionic liquids form linear polymer chains, as demonstrated previously by Marcilla and coworkers.[41] As illustrated in Table 2, these stationary phases exhibited a range of initial separation efficiencies, ranging from 2813 plates/m for ionic liquid **1** and ~1900 plates/m for ionic liquid **3** when conditioned to 120 °C. While it appears that the hexyl-substituted vinylimidazolium cation produces a more efficient stationary-phase coating, subsequent evaluation of the stationary phases using higher conditioning temperatures revealed that the efficiencies of these capillaries decreased rapidly. After conditioning up to 350 °C, volatilization of the ionic liquids resulted in efficiencies that dropped to several hundred plates/m. No retention of naphthalene was observed after conditioning the capillaries to 380 °C, indicating an insufficient amount of ionic liquid remained on the capillary wall.

Performance of Partially Cross-Linked IL Matrix. To produce a more thermally robust ionic liquid matrix, geminal dicationic vinylimidazolium cross-linkers with different length alkyl chains separating the dications were mixed with the monocationic monomers. These mixtures are shown in Table 2 under cross-linked matrixes. From our previous solution-based polymerization experiments, it was found that the concentration of cross-linker is crucial for the formation of a matrix exhibiting ideal stationary-phase properties (data not shown). Compound **4** (see Table 1), is a mixture of three dicationic ionic liquids separated by a six-carbon linkage chain. As discussed in the Experimental Section, electrospray mass spectrometry indicated that, for every one of the 1,6-di(3-methylimidazolium)hexane [$C_6(mim)_2^{2+}$] dications and 1,6-di(3-vinylimidazolium)hexane [$C_6(vim)_2^{2+}$] dications, there are two of the 1-(3-vinylimidazolium)-6-(3′-methylimidazolium)hexane [$C_6vm(im)_2^{2+}$] dications. When a column was prepared by polymerizing only this mixture, the initial efficiency after conditioning to 120 °C was nearly 3000 plates/m (Table 2). Moreover, the efficiency dropped much less after conditioning the capillary at higher temperatures. For example, the efficiency of **4** after conditioning at 350 °C was 1365 plates/m whereas the efficiencies of the monocationic linear IL polymers without cross-linker ranged from 120 to 197 plates/m after the same conditioning step. Clearly, by cross-linking the ionic liquids, the efficiency and thermal stability of the stationary phase is preserved at higher temperatures.

Because of the aforementioned results, a series of different cross-linked ILs were synthesized using various ratios of 1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl] imidate (**1**) and the dication mixture **4**, described above. The highest efficiencies were obtained with cross-linking mixtures formed with equal percentages of the monocationic and cross-linking monomers whereas copolymers formed with a higher concentration of cross-linker exhibited lower efficiencies.

The effect of the alkyl side chain of the monocationic monomer was investigated by preparing equal molar ratios of the cross-linking mixture **4** with two other monocationic monomers, 1-vinyl-3-nonylimidazolium bis[(trifluoromethyl)sulfonyl]imidate (**2**) and 1-vinyl-3-dodecylimidazolium bis[(trifluoromethyl)sulfonyl]imidate **(3)**. As Table 2 illustrates, there is very little difference between these different composition cross-linked matrixes in terms of separation efficiency and loss of efficiency at high temperatures. Recall that previously it was noted that when the monocationic linear IL matrixes were formed, the length of the alkyl group appeared to have an effect on the separation efficiency/thermal stability of the stationary phase at higher temperatures. By forming

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Table 3. Effect of AIBN Initiator Concentration[a] on Efficiency (Theoretical Plates/Meter) as a Function of Conditioning of the Cross-Linked Stationary Phase

	partially cross-linked ionic liquid matrix				cross-linked ionic liquid matrix			
	0.10% **2** 0.10% **5** 0.5% AIBN	0.10% **2** 0.10% **5** 3.5% AIBN	0.10% **2** 0.10% **5** 7.0% AIBN	0.10% **2** 0.10% **5** 10.0% AIBN	0.20% $C_{9-12}(vim)_2$-NTf_2 0.5% AIBN	0.20% $C_{9-12}(vim)_2$-NTf_2 3.5% AIBN	0.20% $C_{9-12}(vim)_2$-NTf_2 7.0% AIBN	0.20% $C_{9-12}(vim)_2$-NTf_2 10.0% AIBN
30−120 °C 3 °C/min hold 2 h	3296	3566	3831	3817	3426	3155	2792	2905
100−200 °C 3 °C/min hold 5 h	3215	3277	3703	3529	2697	2379	2275	2309
150−250 °C 3 °C/min hold 3 h	3090	3016	3069	3027	1723	1598	1682	1398
200−285 °C 3 °C/min hold 2 h	2210	2536	2375	2559	950	771	865	649
200−300 °C 3 °C/min hold 1 h	1317	2024	2298	2009	676	554	768	603
200−350 °C 3 °C/min hold 1 h	112	146	598	1214	1593	950	1664	1506
285−385 °C 3 °C/min hold 20 min			140	68	178	239	490	453

[a] The percentage of AIBN initiator indicated is based on the weight percent of the ionic liquid.

Table 4. Comparison of Solvation Thermodynamics of One Neat and Two Cross-Linked ioNic Liquids

			partially cross-linked IL			neat monomeric IL			mostly cross-linked IL		
	temp range (°C)		0.10% nvim-NTf_2 (**2**) 0.10% $C_9(vim)_2$-NTf_2 (**5**) 3.5% AIBN			0.20% nmim-NTf_2 (**9**)			0.20% $C_{9-12}(vim)_2$-NTf_2[a] 3.5% AIBN		
probe molecule	min	max	ΔG (J/mol)	ΔH_{AV}[b] (J/mol)	ΔS_{AV}[c] (J/mol K)	ΔG (J/mol)	ΔH_{AV}[b] (J/mol)	ΔS_{AV}[c] (J/mol K)	ΔG (J/mol)	ΔH_{AV}[b] (J/mol)	ΔS_{AV}[c] (J/mol K)
fluorophenol	40	100	−6071 (70 °C)	−49308 ±31.0	−126 ±2.3	−6583 (70 °C)	−48104 ±79.5	−121 ±0.25	−5429 (70 °C)	−48323 ±482.7	−125 ±1.52
naphthalene	40	100	−10087 (70 °C)	−54353 ±23.7	−129 ±0.67	−10209 (70 °C)	−53789 ±91.0	−127 ±0.31	−8902 (70 °C)	−52825 ±52.3	−128 ±0.15
2-chloroaniline	40	100	−11320 (70 °C)	−56616 ±18.1	−132 ±0.06	−11670 (70 °C)	−57652 ±57.5	−134 ±0.17	−10064 (70 °C)	−57075 ±63.4	−137 ±0.21
ethyl phenyl ether	35	75	−7058 (50 °C)	−46482 ±140	−122 ±0.52	−7420 (50 °C)	−46521 ±69.0	−121 ±0.21	−5622 (50 °C)	−46662 ±409	−127 ±1.31
1-octanol	35	75	−10433 (50 °C)	−59229 ±50.7	−151 ±0.23	−10481 (50 °C)	−59277 ±58.2	−151 ±0.44	−8213 (50 °C)	−56039 ±58.1	−148 ±0.15
decane	35	75	−4457 (50 °C)	−45497 ±363	−127 ±1.5	−4349 (50 °C)	−45389 ±138	−127 ±0.46	−1813 (50 °C)	−46408 ±98.7	−138 ±3.52
nitropropane	27	50	−5220 (35 °C)	−38808 ±49.5	−109 ±0.17	−5422 (35 °C)	−39010 ±312	−109 ±1.0	−4367 (35 °C)	−38263 ±198	−110 ±0.60

[a] This mixture consists of a combination of a homologous series of ionic liquids that are 10.88 wt % **5**, 9.29% **6**, 19.59% **7**, and 60.24% **8**. [b] Represents the average standard enthalpy change as determined by triplicate measurement of the probe molecule retention factor. [c] Represents the average standard entropy change as determined by triplicate measurement of the probe molecule retention factor.

a cross-linked stationary phase, it is observed that the length of the alkyl group on the monocationic monomer plays less of a role in the loss of separation efficiency at high temperatures.

Performance of Highly Cross-linked IL Matrixes. Ionic liquid stationary phases based only on the cross-linking monomers were also evaluated. As shown in Table 2, one mixture was based on the cross-linking of vinylimidazolium dications separated by a nonane linkage chain (0.20% **5**) while the second mixture consisted of ionic liquids **5**, **6**, **7**, and **8**, namely, dicationic ionic liquid monomers separated by a nonane, decane, undecane, and dodecane linkage chain, respectively. This mixture of four cross-linkers, abbreviated as $C_{9-12}(vim)_2$-NTf_2 in Table 4, was made due to the fact that **6** and **8** are supercooled liquids at room temperature and, therefore, are not ideal monomers for creating "gummy" or "waxy" stationary phases. This mixture consists of 10.88 wt % **5**, 9.29% **6**, 19.59% **7**, and 60.24% **8**.

A couple interesting trends were observed for the highly cross-linked ionic liquid stationary phases that were not observed for the linear monocationic or partially cross-linked materials. First, although the separation efficiency of the highly cross-linked stationary phases was low after conditioning to 380 °C, the ionic liquid stationary phase was still present as a thin film in the capillary when viewed under microscope after prolonged exposure to this temperature. In contrast, only a few partially cross-linked

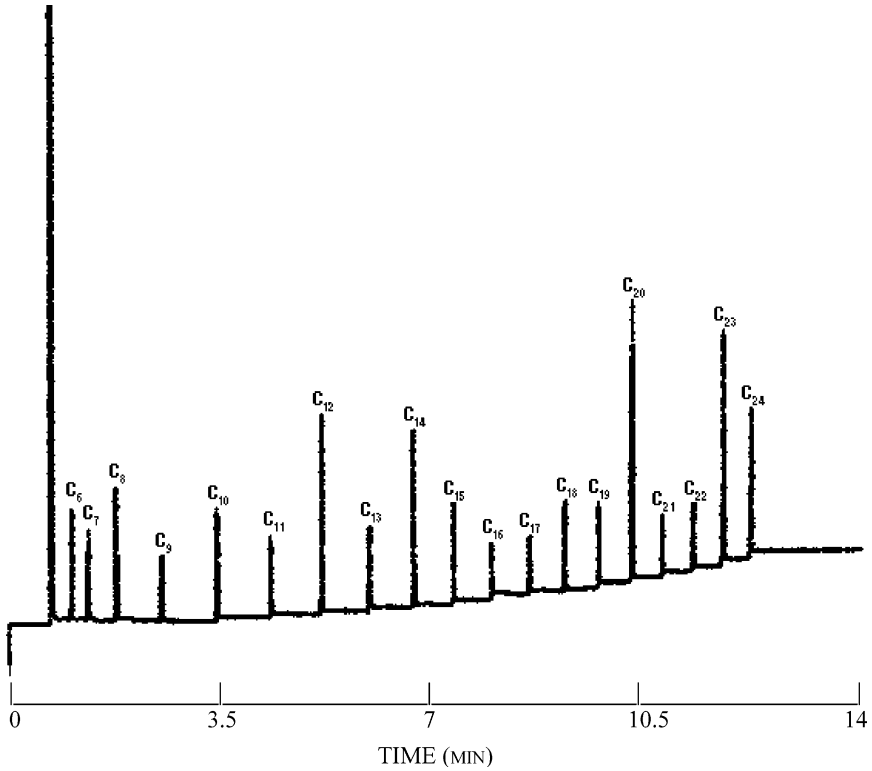

Figure 3. Separation of fatty acid methyl esters (C_6-C_{24}) on a 15-m partially cross-linked ionic liquid stationary phase (0.10% nvim-NTf_2 **(2)**/10% $C_9(vim)_2$-NTf_2 **(5)** with 7.5% AIBN). Conditions: 100 °C hold 2 min, 15 °C/min to 260 °C.

stationary phases and no monocationic linear IL stationary phases provided retention of naphthalene after high-temperature conditioning.

The most impressive and interesting characteristic of the completely cross-linked ionic liquid stationary phases is their apparent ability to exhibit a substantial increase in efficiency after conditioning at high temperatures. Examples of this are found in Table 2 under the heading cross-linked ionic liquid matrix. In one such example, a cross-linked matrix previously described containing a mixture of four dicationic cross-linkers, $C_{9-12}(vim)_2$-NTf_2, was formed and the efficiency of this stationary phase was observed to undergo a 200−250% increase when the column was conditioned from 300 to 350 °C (see Table 2). This trend was observed on all highly cross-linked stationary phases examined and appears to be independent of the initial AIBN concentration in the coating solution (see Table 3).

The fact that the efficiencies of the highly cross-linked stationary phases increase in this narrow temperature range is not well understood but certainly makes them very useful for high-temperature separations. One possible explanation may be that, at higher temperatures, slight volatilization/decomposition of the stationary phase occurs causing the film thickness of the stationary phase to gradually decrease, thereby giving rise to the observed higher efficiency. Alternatively, the increase in analyte diffusivity in the stationary phase at high temperatures could improve the efficiency. Clearly, by exhibiting this behavior, these stationary phases appear to exhibit the smallest decrease in efficiency up to temperatures around 350 °C. However, it was observed that when the completely cross-linked stationary phases are used to separate low molecular weight molecules at low temperatures, the separation efficiency is average to poor (see Tables 2 and 3). For low to moderate temperature separations (25−285 °C), the partially cross-linked stationary phases, particularly those containing equal weight percentages of ionic liquids **2** and **5**, provide the highest efficiency separations up to 285 °C with little column bleed at temperatures at and above 250 °C. Meanwhile, the completely cross-linked stationary phases provides the highest efficiency separations with little column bleed up to temperatures around 300−380 °C. Therefore, these two optimized types of immobilized ionic liquid stationary phases are specifically proposed for normal GC temperature ranges and higher GC temperatures, respectively. Low to moderate temperature separations are optimal with partial cross-linking of the stationary phase whereas high-temperature separations require more extensive cross-linking to maintain acceptable efficiency and low column bleed.

Effect of AIBN Initiator Concentration. The two optimized cross-linked stationary phases chosen for the moderate- (0.10% **2** and 0.10% **5**) and high-temperature (0.20% $C_{9-12}(vim)_2$-NTf_2) separations were further studied to determine the effect of AIBN initiator concentration on their separation efficiency and thermal stability. As shown in Table 3, each copolymer was formed using a different concentration of AIBN in the coating solution. These concentrations ranged from 0.5 (w/w of AIBN to ionic liquid) to 10.0%.

For the partially cross-linked stationary phase, a higher weight percentage of initiator results in a slightly more efficient stationary phase (i.e., 3296 plates/m for 0.5% AIBN to 3817 plates/m for 10.0% AIBN). In addition, the efficiencies of the 7.0 and 10.0 wt % initiator copolymers decrease less rapidly at higher temperatures (>250 °C) compared to those IL matrixes produced with lower initiator concentrations. After the stationary phase is subjected to a temperature ramp up to 385 °C, only the two copolymers formed

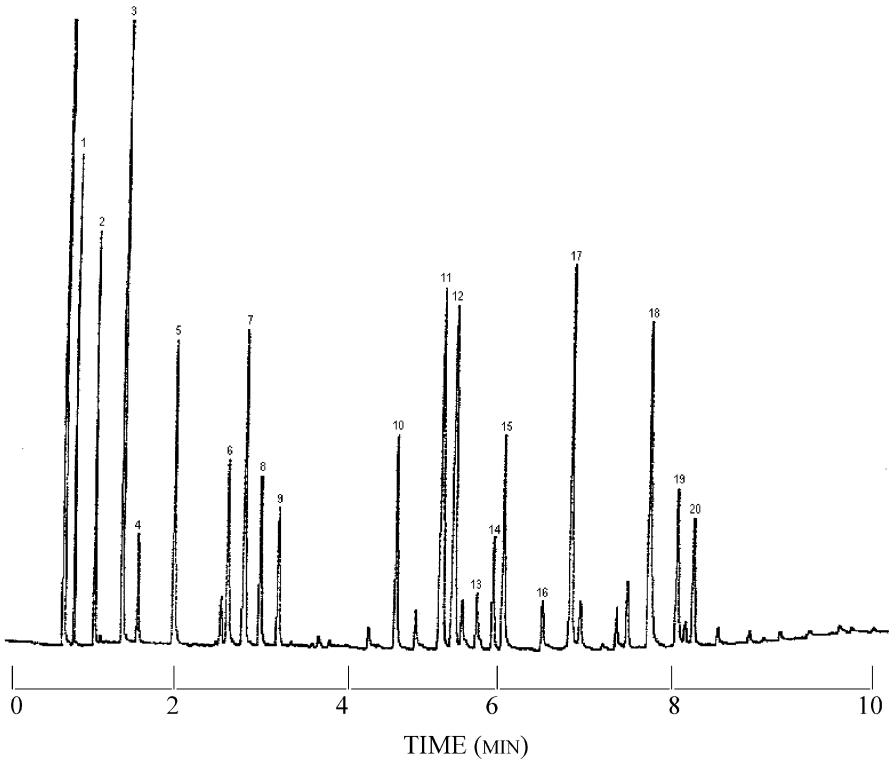

Figure 4. Separation of PAH and chlorinated pesticide mixture on a 13-m $C_9(vim)_2$-NTf_2 (7.5% AIBN) mostly cross-linked ionic liquid stationary phase: 1, indene; 2, naphthalene; 3, biphenyl; 4, azulene; 5, acenaphthene; 6, acenaphthylene; 7, heptachlor; 8, fluorene; 9, BHC; 10, dibenzothiophene; 11, DDE; 12, endosulfan; 13, anthracene; 14, dieldrin; 15, 4*H*-cyclopenta[*def*]phenanthrene; 16, fluoranthene; 17, DDT; 18, lindane; 19, pyrene; 20, carbazole. Conditions: 175 °C for 1 min; 20 °C/min to 335 °C. The smaller, unnumbered peaks in this chromatogram are impurities contained in numbered standard materials.

with 7.0 and 10.0% initiator provide retention of naphthalene, however, with very low efficiency. The other two cross-linked stationary phases were no longer observed in the capillary after high-temperature conditioning (385 °C) and therefore provided no retention.

In the case of the highly cross-linked stationary phase (0.20% $C_{9-12}(vim)_2$-NTf_2), a trend nearly opposite to that observed for the partially cross-linked ionic liquids was observed (Table 3). The efficiencies of the columns after the first conditioning step are higher for the copolymers formed with lower AIBN concentration. However, it was still found that a higher weight percentage of AIBN results in a smaller decrease of efficiency at higher temperatures compared to the copolymers formed with lower percentages of AIBN. All of the highly cross-linked stationary phases were found to retain naphthalene after conditioning at 385 °C.

As discussed previously, the highly cross-linked stationary phases exhibit an increase in the separation efficiency for naphthalene after being conditioned to 350 °C as compared to being conditioned at only 300 °C. The magnitude of this increase does not appear to be directly related to the initiator concentration. For example, the efficiency increase exhibited by the copolymer formed with 3.5% AIBN is ~171% higher after the 350 °C program compared to the 300 °C program whereas that for the 10.0% AIBN is ~250% higher. As previously observed for the partially cross-linked ionic liquids, the overall decrease in efficiency is lowest for copolymers formed with higher AIBN concentrations.

These results, coupled with those from the previous sections, indicate that at high temperatures the most efficient and thermally stable stationary phases appear to be those that are cross-linked with a weight percentage of AIBN equal to or greater than 7.0%. In contrast, for lower/normal temperature separations, the choice of the monocationic monomer and cross-linker plays a more important role in the stationary-phase efficiency and higher initiator concentration tends to prevent large decreases in efficiency with increasing temperature.

Comparison of Solvation Thermodynamics and Interaction Parameters of the Cross-Linked Ionic Liquids and the Neat Ionic Liquid Stationary Phases. It has been demonstrated previously that room-temperature ionic liquids act as broadly applicable, superb gas chromatographic stationary phases in that they exhibit a dual nature retention behavior.[21,25,35] Consequently, ionic liquid stationary phases have been shown to separate, with high efficiency, both polar and nonpolar molecules on a single column. By producing stationary phases that are either partially or highly cross-linked, it is of interest to ensure that the solvation thermodynamics and solvation interactions inherent to ionic liquids are still retained by their immobilized analogues.

Solvation Thermodynamics. The solvation thermodynamics (Table 4) for the two optimized cross-linked and a neat ionic liquid were determined as previously described in the Experimental Section. As can be seen from the data in these tables, the free energy of transfer of solute is similar for both the cross-linked and neat monomeric IL stationary phases. While the enthalpies of solvation for all probe molecules differed only slightly between the three ionic liquids, a larger difference was observed for the entropies of solvation on the highly cross-linked stationary phase for certain solutes, i.e., 2-chloroaniline, ethyl phenyl ether, and

Table 5. Comparison of Interaction Parameters of One Neat and Two Cross-Linked Ionic Liquids

temp (°C)	interaction parameters[a]								
	c	*r*	*s*	*a*	*b*	*l*	*n*	R^2	*F*
	0.20% nmim-NTf_2 (**9**)								
40	−2.98	0	1.62	1.91	0.36	0.75	32	0.99	477.86
	(0.11)	(0.09)	(0.10)	(0.10)	(0.13)	(0.03)		(0.10)	
70	−3.05	0	1.54	1.57	0.18	0.63	32	0.99	660.78
	(0.08)	(0.07)	(0.07)	(0.07)	(0.10)	(0.02)		(0.07)	
100	−3.47	0	1.52	1.43	0.12	0.60	30	0.99	304.17
	(0.11)	(0.09)	(0.10)	(0.09)	(0.13)	(0.03)		(0.09)	
	0.10% C_9(vim)-NTf_2 (**2**); 0.10% $C_9(vim)_2$-NTf_2 (**5**); 3.5% AIBN								
40	−2.95	0	1.60	1.84	0.45	0.71	32	0.99	404.82
	(0.11)	(0.10)	(0.11)	(0.10)	(0.15)	(0.03)		(0.10)	
70	−3.05	0	1.57	1.53	0.37	0.60	32	0.99	639.52
	(0.08)	(0.07)	(0.08)	(0.07)	(0.10)	(0.02)		(0.07)	
100	−3.49	0	1.54	1.41	0.31	0.54	30	0.98	299.60
	(0.12)	(0.09)	(0.11)	(0.09)	(0.14)	(0.03)		(0.09)	
	0.20% $C_{9-12}(vim)_2$-NTf_2;[b] 3.5% AIBN								
40	−3.31	0	1.92	1.94	0.59	0.68	32	0.99	573.26
	(0.10)	(0.09)	(0.10)	(0.09)	(0.13)	(0.03)		(0.09)	
70	−3.55	0	1.88	1.71	0.46	0.59	32	0.99	305.25
	(0.12)	(0.10)	(0.11)	(0.09)	(0.15)	(0.03)		(0.10)	
100	−3.65	0	1.73	1.46	0.32	0.48	30	0.98	254.83
	(0.13)	(0.11)	(0.13)	(0.12)	(0.18)	(0.04)		(0.11)	

[a] *r*, interaction via nonbonding and π-electrons; *s*, dipolarity/polarizability; *a*, hydrogen-bond basicity; *b*, hydrogen-bond acidity; *l*, dispersion forces; *n*, number of probe molecules subjected to multiple linear regression analysis; R^2, statistical correlation coefficient; *F*, Fisher coefficient. Values in parentheses are the standard deviations for each interaction parameter. [b] This mixture consists of a combination of a homologous series of ionic liquids that are 10.88 wt % **5**, 9.29% **6**, 19.59% **7**, and 60.24% **8**.

decane. The entropies of solvation were somewhat more negative for these molecules indicating that they are part of a more ordered environment with the highly cross-linked stationary phase. These results also indicate that solvation by these three ionic liquid-based stationary phases has a substantial entropic component that contributes to large differences in solute free energy of transfer (see values for 2-chloroaniline and decane in Table 4).

Solvation Interactions. The solvation interaction parameters given in Table 5 indicate that the neat and two cross-linked ionic liquids are very similar in terms of selectivity. All three stationary phases interact weakly via nonbonding and π-electrons (*r*-term). The hydrogen-bond basicity (*a*) and dispersion forces (*l*) were the same within experimental error for all three stationary phases. The partially cross-linked and neat ionic liquids possessed the same magnitude of dipolar interactions, which were somewhat lower than those exhibited by the highly cross-linked ionic liquid. Within experimental error, all three ionic liquids possessed the same ability to undergo hydrogen-bond acidity (*b*) interactions.

Chromatographic Performance of the Partially and Highly Cross-Linked Ionic Liquid Stationary Phases. Previously, we demonstrated the unique selectivity of ionic liquid stationary phases in the separation of a wide variety of analyte molecules including alcohols, alkanes, PAHs, polychlorinated biphenyls (PCBs), and chlorinated pesticides.[25] The fact that the selectivity of the ionic liquid stationary phases is preserved after cross-linking the matrix is demonstrated in Figures 3 and 4. Figure 3 shows a separation of 19 FAMEs on a 15-m column coated with a partially cross-linked IL stationary phase. This separation is performed in 12 min using the temperature ramp described. Figure 4 illustrates the separation of a mixture of PAHs and chlorinated pesticides on a 12-m highly cross-linked stationary phase. The 9-min, high-temperature GC separation is carried out using a temperature program up to 335 °C with little observed column bleed. While the selectivity of these ionic liquids is little different from that observed previously with the neat ionic liquids,[25] the fact that separations can now be accomplished at higher temperatures with little column bleed, high efficiency, and little shifting of the retention time after exposure to extreme temperatures further demonstrates the effectiveness of the immobilized ionic liquid.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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